

WHAT IS CLAIMED IS:

1. A process for the desulfurization of a hydrocarbonaceous oil which process

comprises:

(a) contacting the hydrocarbonaceous oil with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone at hydrodesulfurization conditions to produce hydrogen sulfide and a resulting first hydrocarbonaceous oil stream having a reduced concentration of sulfur;

(b) contacting the first hydrocarbonaceous oil stream having a reduced concentration of sulfur with an aqueous oxidizing solution in an oxidation zone to produce a second hydrocarbonaceous oil stream comprising sulfur-oxidated compounds;

(c) contacting the second hydrocarbonaceous stream comprising sulfur-oxidated compounds from step (b) with a selective adsorbent having a greater selectivity for the sulfur-oxidated compounds than for sulfur-free hydrocarbonaceous oil to produce an adsorbent containing at least a portion of the sulfur-oxidated compounds and a third hydrocarbonaceous oil stream having a reduced concentration of sulfur-oxidated compounds;

(d) separating the adsorbent containing at least a portion of the sulfur-oxidated compounds produced in step (c) to provide an adsorbent rich in sulfur-oxidated compounds; and

(e) recovering the third hydrocarbonaceous oil stream.

2. The process of claim 1 wherein the hydrocarbonaceous oil boils in the range from about 149°C (300°F) to about 538°C (1000°F).
3. The process of claim 1 wherein the hydrodesulfurization reaction zone is operated at conditions which include a pressure from about 800 kPa (100 psig) to 5 about 12.5 MPa (1800 psig), a maximum catalyst temperature from about 204°C (400°F) to about 400°C (750°F) and a hydrogen to feed ratio from about 33.7 nm<sup>3</sup>/m<sup>3</sup> (200 SCFB) to about 1685 nm<sup>3</sup>/m<sup>3</sup> (10,000 SCFB).
4. The process of claim 1 wherein the hydrodesulfurization catalyst comprises a Group VIB metal component, a Group VIII metal component and alumina.
- 10 5. The process of claim 1 wherein the hydrocarbonaceous oil stream having a reduced concentration of sulfur and produced in step (a) has a sulfur level from about 100 ppm to about 1000 ppm.
6. The process of claim 1 wherein the sulfur-oxidated compounds are selected from the group consisting of sulfoxide and sulfones.
- 15 7. The process of claim 6 wherein the oxidizing agent is selected from the group consisting of a gas, a liquid and a solid.
8. The process of claim 1 wherein the oxidizing agent is selected from the group consisting of oxygen, ozone, nitrogen oxide, hydrogen peroxide, organic hydroperoxide, carboxylic peracids and metal superoxides.
- 20 9. The process of claim 1 wherein the oxidation zone contains an oxidation catalyst.

10. The process of claim 1 wherein at least a portion of any residual oxidizing solution from the step (b) is decomposed.

11. The process of claim 10 wherein the decomposition is conducted in the presence of a catalyst.

5 12. The process of claim 1 wherein the aqueous oxidizing solution comprises hydrogen peroxide and a carboxylic acid.

13. The process of claim 12 wherein the oxidation zone is operated at conditions including a molar feed ratio of hydrogen peroxide to sulfur ranging from about 1 to about 10 and a molar ratio of carboxylic acid to hydrogen peroxide from about 0.1 to 10 about 10.

14. The process of claim 1 wherein the oxidation zone is operated at conditions including a pressure from about atmospheric to about 800 kPa (100 psig) and a temperature from about 38°C (100°F) to about 149°C (300°F).

15. The process of claim 1 wherein the selective adsorbent is selected from the group consisting of silica, alumina, silicalite, ZSM-5, zeolite L, X and Y-type zeolites, dealuminated Y-type zeolite, zeolite beta, zeolite omega, and SAPO-34.

16. The process of claim 1 wherein the contacting in step (c) is selected from the group of consisting of fixed bed, ebullated bed, fluidized bed, or counter current solid-liquid contacting.

20 17. A process for the desulfurization of a hydrocarbonaceous oil which process comprises:

- a) contacting the hydrocarbonaceous oil with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone at hydrodesulfurization conditions to produce hydrogen sulfide and a resulting first hydrocarbonaceous oil stream having a reduced concentration of sulfur;
- 5 b) contacting the first hydrocarbonaceous oil stream having a reduced concentration of sulfur with an aqueous oxidizing solution in an oxidation zone to produce a second hydrocarbonaceous stream oil stream comprising sulfur-oxidized compounds;
- c) contacting the second hydrocarbonaceous stream comprising sulfur-oxidized compounds from step (b) with a selective adsorbent having a greater selectivity for the sulfur oxidized compounds than for sulfur-free hydrocarbonaceous oil to produce an adsorbent containing at least a portion of the sulfur-oxidized compounds and a third hydrocarbonaceous oil stream having a reduced concentration of sulfur-oxidized compounds;
- 10 d) separating the adsorbent containing at least a portion of the sulfur-oxidized compounds produced in step (c) to provide an adsorbent rich in sulfur-oxidized compounds;
- e) regenerating at least a portion of the adsorbent from step (d) and recycling to step (c) to provide at least a portion of the selective adsorbent, and;
- 15 f) recovering the third hydrocarbonaceous oil stream.

18. The process of claim 17 wherein at least a portion of any residual oxidizing solution from the step (b) is decomposed.

19. The process of claim 17 wherein the hydrodesulfurization reaction zone is operated at conditions which include a pressure from about 800 kPa (100 psig) to about 12.5 MPa (1800 psig), a maximum temperature from about 204°C (400°F) to about 400°C (750°F) and a hydrogen to feed ratio from about 33.7 nm<sup>3</sup>/m<sup>3</sup>

5 (200 SCFB) to about 1685 nm<sup>3</sup>/m<sup>3</sup> (10,000 SCFB).

20. The process of claim 17 wherein the aqueous oxidizing solution comprises hydrogen peroxide and a carboxylic acid.

21. The process of claim 20 wherein the oxidation zone is operated at conditions including a molar feed ratio of hydrogen peroxide to sulfur ranging from about 1 to 10 about 10 and a molar ratio of carboxylic acid to hydrogen peroxide from about 0.1 to about 10.

22. The process of claim 17 wherein the process of claim 1 wherein the selective adsorbent is selected from the group consisting of silica, alumina, silicalite, ZSM-5, zeolite L, X and Y-type zeolites, dealuminated Y-type zeolite, zeolite beta, zeolite

15 omega, and SAPO-34.

23. A process for the desulfurization of a hydrocarbonaceous oil which process comprises:

a) contacting the hydrocarbonaceous oil boiling in the range from about 149°C (300°F) to about 538°C (1000°F) with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone at hydrodesulfurization conditions which include a pressure from about 800 kPa (100 psig) to about 12.5 MPa

(1800 psig), a maximum temperature from about 204°C (400°F) to about 400°C (750°F) and a hydrogen to feed ratio from about 33.7 nm<sup>3</sup>/m<sup>3</sup> (200 SCFB) to about 1685 nm<sup>3</sup>/m<sup>3</sup> (10,000 SCFB) to produce hydrogen sulfide and a resulting first hydrocarbonaceous oil stream having a reduced concentration of sulfur;

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b) contacting the first hydrocarbonaceous oil stream having a reduced concentration of sulfur with an aqueous oxidizing solution comprising acetic acid and hydrogen peroxide in an oxidation zone to produce a second hydrocarbonaceous oil stream comprising sulfur-oxidated compounds;

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c) decomposing at least a portion of any residual oxidizing solution from the sulfur oxidation effluent;

d) contacting an effluent stream from step (c) comprising sulfur-oxidated compounds with a selective adsorbent selected from the group consisting of silica, alumina, silicalite, ZSM-5, zeolite L, X and Y-type zeolites, dealuminated Y-type zeolite, zeolite beta, zeolite omega and SAPO-34, and having a greater selectivity for the sulfur oxidized compounds than for sulfur-free hydrocarbonaceous oil to produce an adsorbent containing at least a portion of the sulfur-oxidated compounds and a third hydrocarbonaceous oil stream having a reduced concentration of sulfur-oxidated compounds;

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e) separating the adsorbent containing at least a portion of the sulfur-oxidated compounds produced in step (d) to provide an adsorbent rich in sulfur-oxidated compounds;

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- f) regenerating at least a portion of the adsorbent from step (e) and recycling to step (d) to provide at least a portion of the selective adsorbent, and;
- g) recovering the third hydrocarbonaceous oil stream.